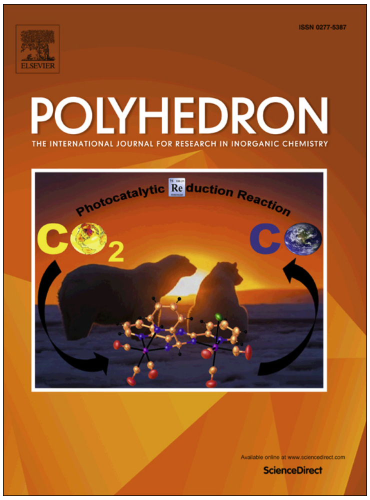

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For table of contents use only

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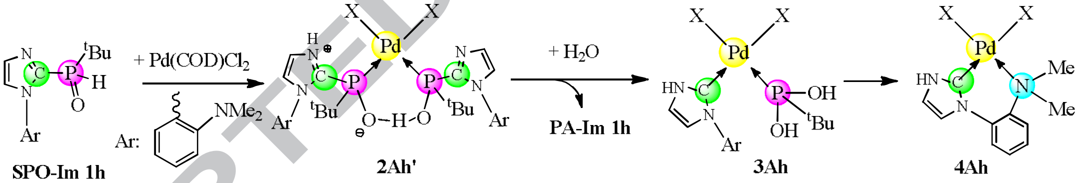
The reaction of SPO-Im **1h** with $Pd(COD)Cl_2$ yielded a *bis*-**1h'** (PA-Im) coordinated *cis*-palladium dichloride complex, **2Ah'**. It subsequently converted to a carbene coordinated palladium complex, **3Ah**, in the presence of moisture, and eventually to **4Ah**. The P-C(imidazole) bond of **1h'** was dissected and the dissociated species acted as a NHC carbene ligand towards palladium metal.



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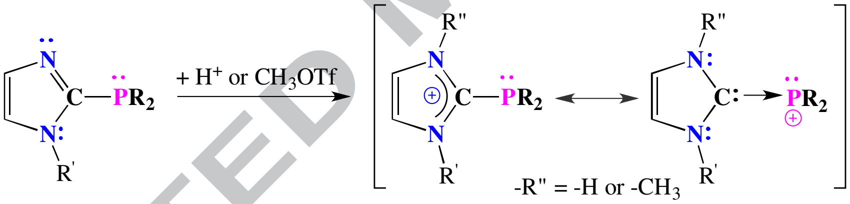
Abstract: New pre-ligands of 1-aryl-1*H*-imidazol-2-yl substituted secondary phosphine oxides (HRP(=O)-Im: SPO-Im) were prepared and characterized by spectroscopic means. The SPO-Im pre-ligands are able to tautomerize to their corresponding genuine ligands, the 1-aryl-1*H*-imidazol-2-yl substituted phosphinous acids ((HO)RP-Im: PA-Im) while the condition permitted. Further reactions of selected SPO-Im pre-ligands toward Pd(COD)Cl_2 or PdBr yielded *bis*-(PA-Im)-coordinated *cis*-palladium dichloride or dibromide complexes, respectively. These *cis*-palladium dihalide complexes are all having an intramolecular hydrogen bond between two coordinated PA-Im ligands (R(Im(H)$^+$)P-O$^{-}\cdots$HO-PRIm) by transfering a proton from one of the two P-OH groups to its free nitrogen site of imidazolyl substituents; and, therefore, imposes the formation of zwitterionic *cis*-form palladium complexes. Three crystal structures of these square-planar zwitterionic palladium complexes were determined by the X-ray diffraction methods. Additionally, two novel NHC carbene coordinated palladium complexes were obtained from the crystal-growing process of the above-mentioned zwitterionic *cis*-palladium dihalide complexes. The crystal structures of two NHC carbene coordinated palladium complexes were also successfully determined. Density-functional theory (DFT) calculations were carried out to substantiate the feasibility of the proposed reaction pathways for the formation of NHC carbene coordinated palladium complexes. Finally, applying selected SPO-Im pre-ligands to Heck reactions with pre-optimized reaction conditions exhibited satisfactory performances.

Keywords: Nitrogen Heterocyclic Carbene (NHC) • Secondary Phosphine Oxide (SPO) • Palladium • Heck reaction • Density Functional Theory (DFT)

1. Introduction

Various types and functions of organophosphines have probably been the most employed ligands in transition-metal complexes catalyzed reactions, particularly in cross-coupling reactions.[1] Nevertheless, these tri-substituted organophosphine ligands often create practical problems of being sensitive towards air and moisture and eventually loss their coordinating capacities.[2] Thereby, other air-stable heterocyclic ligands such as pyridines,[3] quinolines,[4] imidazoles,[5] tetrazoles,[6] oxazolines,[7] Schiff bases and hydrazones,[8] were introduced as alternative solutions. Particularly, N-heterocyclic carbenes (NHCs) have merged recently as one of the most prestigious competitors among non-phosphine ligands. Moreover, methods for the preparation of phosphines,[9] NHCs[10] and the hybrid of these two types of ligands[11] have been reported and their catalytic performances were examined.

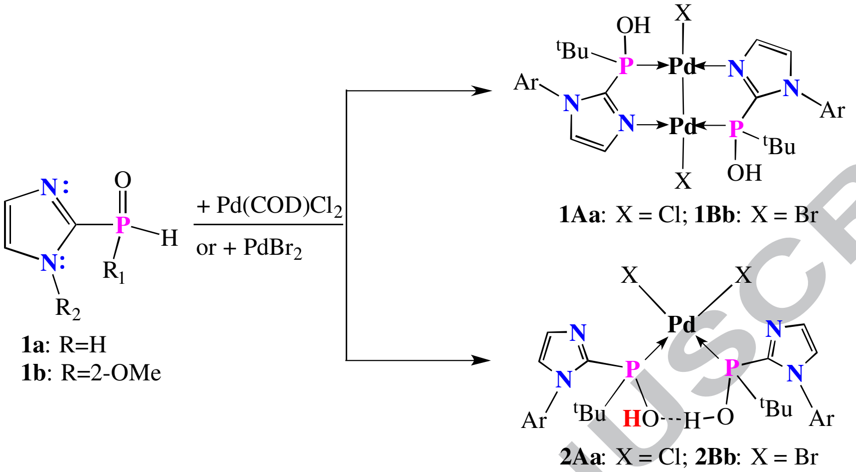
Recently, a fascinating category of phosphine ligands having the general form of PR_2-Im (Im: imidazolyl) has been developed (Scheme 1). For PR_2-Im, protonation or alkylation on lone pair of nitrogen atom of imidazolyl ring can give rise to cationic and dative-bond featured phosphenium-NHC species ($PR_2^+ \leftarrow$NHC, NHC: N-heterocyclic carbene)[12] capable of acting as potential carbene-transfer reagent.[13] For instance; an NCH-coordinated gold complex was obtained from the reaction of AuCl←(PR_2-Im) complex with methanol (proton and weak nucleophile source).[14] Note that the $PR_2(OMe)$ byproduct is still a potential ligand for metal coordination. Thus, protonated or alkylated phosphenium-NHC can be regarded as a two-in-one compound ligating system.



Scheme 1. Illustration of chemical transformation for PR_2-Im to $PR_2^+ \leftarrow$NHC adduct.

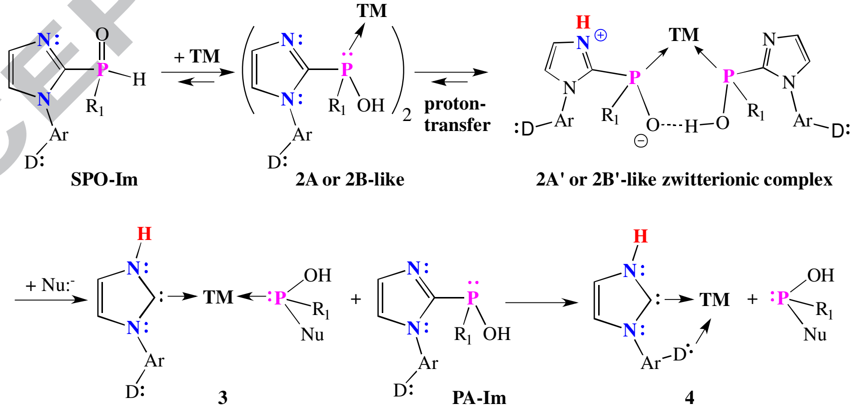
In ligand-assisted transition-metal catalyzed reactions, the application of secondary phosphine oxides as pre-ligands (SPOs, RR'P(O)H) has attracted much attention due both to their thermal- and air-stability.[15] As demonstrated repeatedly, the coordinating capacity of SPO towards transition metal is acquired through tautomerization, in which the P(V) in RR'P(O)H is converted to P(III) in phosphinous acid (PA, RR'POH) in solution.[16] The PA tautomer is having a lone pair of electrons and functioning as authentic phosphine ligand in coordination chemistry.

Previously, we had demonstrated that SPO-imidazolios **1a** and **1b** are active SPO pre-ligands for Suzuki-Miyaura cross-coupling reactions (Scheme 2).[17] These SPO-based pre-ligands **1a** and **1b** are symbolized as SPO-Im, which is analogous to the neutral PR_2-Im.[17] Herein, we show that palladium complex **2Aa** can be obtained by treating **1a** with $Pd(COD)Cl_2$; while **2Bb** was synthesized from the reaction of **1b** with $PdBr_2$ (Scheme 2). Their crystal structures were determined by X-ray diffraction methods. More interestingly, two unconventional dinuclear Pd(I)-Pd(I) complexes, **1Aa** and **1Bb**, were also obtained from these two reactions of **1a** and **1b**, respectively.[17] In the literature, only few palladium complexes Pd(I)-Pd(I) were reported.[18] Therefore, as shown in Scheme 2 and referenced from literature, the resulted palladium complexes in our studies were classified into two categories: (i) dinuclear Pd(I)-Pd(I) complexes **1Aa** and **1Bb**; [17,18] and (ii) *cis*-form Pd(II) complexes **2Aa** and **2Bb**.[19]



Scheme 2. Reactions of pre-ligand SPO-Im **1a** with Pd(COD)Cl$_2$ and **1b** with PdBr$_2$.[17] The abbreviations of the species are as follows: **Aa** indicates products obtained from the reaction of **1a** + Pd(COD)Cl$_2$, while **Bb** denotes products from **1b** + PdBr$_2$.

On the other hand, palladium-catalyzed coupling of olefins with aryl and vinyl halides, known as Heck reaction,[20] is one of the most important methods to the formation of substituted double bond in organic synthesis.[20j,21] Heck reaction has been proven to be a rather versatile method in the syntheses of important building blocks in pharmaceuticals and bioactive compounds, natural products, monomers, herbicides and high performance materials.[1i,5a,20f,20j,21b,22]



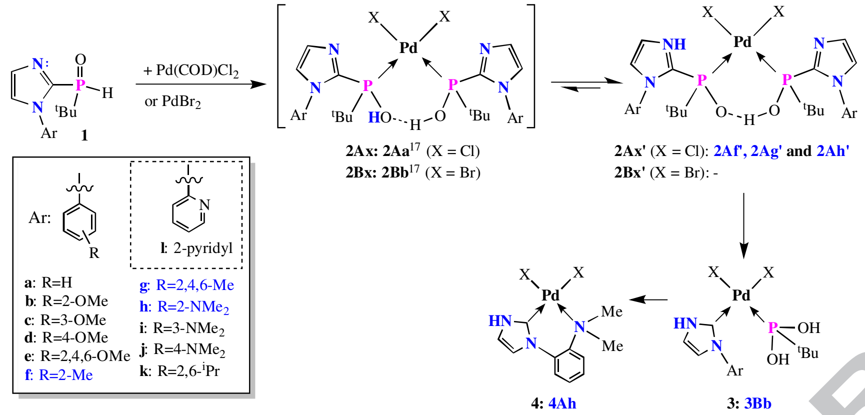
Scheme 3. Potential mode-of-coordination for two-in-one SPO-Im ligating system in the presence of nucleophile. Lone-pair electrons of oxygen atom are not shown for clarity. Ar is a molecular linker and D is a metal-coordinating site, if any.

Herein, we wish to report the preparations of a number of new pre-ligands of SPO-Im **1c-1l** and the related palladium complexes (zwitterionic complex **2'** and neutral complexes **3** and **4** shown in Scheme 3). In comparison with the stable carbene-transfer analogue of NHC-phosphenium oxide or sulfide with non-coordinating pentavalent phosphorus,[23] $[P(=Y)R_2\text{-NHC}]^+$ (Y = O or S), SPO-Im **1**s are potential pre-ligands for metal-coordination (complex **2’** in Scheme 3) and catalysis. It is closely related to the SPO-to-PA (RR'P(O)H to RR'POH) tautomerization that creating a trivalent phosphorus atom in phosphine-like PA ligand. Upon nucleophilic attack on P(III) atom of zwitterionic PA ligand in complex **2’**, the NHC and phosphite-coordinated complex **3** could be obtained. Thus, we are demonstrating here that SPO-Im **1** could act as two-in-one pre-ligands (PA and NHC). If the substituent on nitrogen atom of imidazolyl ring is equipped with an extra coordinating site, complex **3** could dissociate a phosphite ligand to yield complex **4** (Scheme 3). In addition, DFT methods were employed to probe the probable reaction pathways for the formation of unexpected carbene-coordinated palladium complex (**3Aa**) from the reaction of SPO-Im **1a** with $Pd(COD)Cl_2$. Selected SPOs as efficient mono- or bi-dentate pre-ligands in palladium-catalyzed Heck reactions were also investigated.

II. Results and Discussion

Preparation of SPO-Im 1c-1l and the unexpected observations from the reactions with palladium salts

Several new SPO-Im **1c-1l** were prepared according to the procedures modified from our previous work.[17] Firstly, 1-aryl-1*H*-imidazole was prepared by Cu(I)-catalyzed coupling reaction between imidazole and the matching substituted bromobenzene. The first resultant intermediate was then treated with BuLi and $P(^tBu)Cl_2$. Finally, the second intermediate containing one P-Cl bond was followed by hydrolysis work-up in acidic media. Notably, *cis*-form of *bis*-PA coordinated palladium complexes **2Af’**, **2Ag’**, **2Ah’** and **4Ah** can be successfully obtained from the reactions of corresponding pre-ligands of SPO-Im **1f**, **1g**, and **1h** with $Pd(COD)Cl_2$ (Scheme 4). Another palladium complexes **3Bb** that bearing NHC and phosphite ligands was yielded from the reaction of SPO-Im **1b** with $PdBr_2$ (Scheme 4). These palladium complexes were all synthesized with half molar equivalent of PdX_2 (X = Cl or Br) at 25 °C for two hours. It is believed that the formations of **2Ax’** and **2Bx’** were from the tautomerization of their corresponding tautomers **2Ax** and **2Bx**, respectively.[17]



Scheme 4. Reactions of pre-ligands SPO-Im **1**s with Pd(COD)Cl_2 or $PdBr_2$. The abbreviations for the species are as follows: **A** is for X = Cl; **B** is for X = Br; lowercases **a**-**l** are for substituents on either phenyl or pyridyl ring. SPO-Im **1c**-**1k** were newly synthesized in this work, while SPO-Im **1a**-**1b** and palladium complexes **2Aa'** and **2Bb'** were published in ref. [17]. SPO-Im **1b**, **1f**, **1g**, and **1h** (in blue) were employed to synthesize palladium complexes, respectively. Names of complexes indicate the obtained species from their respective reactions.

The structures of three *cis*-form complexes, **2Af'**, **2Ag'** and **2Ah'**, were determined by X-ray diffraction methods. As shown in Figure 1, a hydrogen bonding between O(1)-H(1)···O(2) is present in each case. Compared with the bonding modes of conventional tri-substituted phosphines toward metals, this manner is quite unique for these *cis*-form of *bis*-phosphine ligands coordinated palladium complexes.[5] Interestingly, the released H^+ dissociated from one of the SPOs is relocated to the nitrogen atom of imidazole, forming zwitterionic type complexes **2Af'**, **2Ag'** and **2Ah'**.[24] Thereby, it is believed that the conversion of **2Ax** to its more stable tautomer **2Ax'** shall take place in solution.[25]

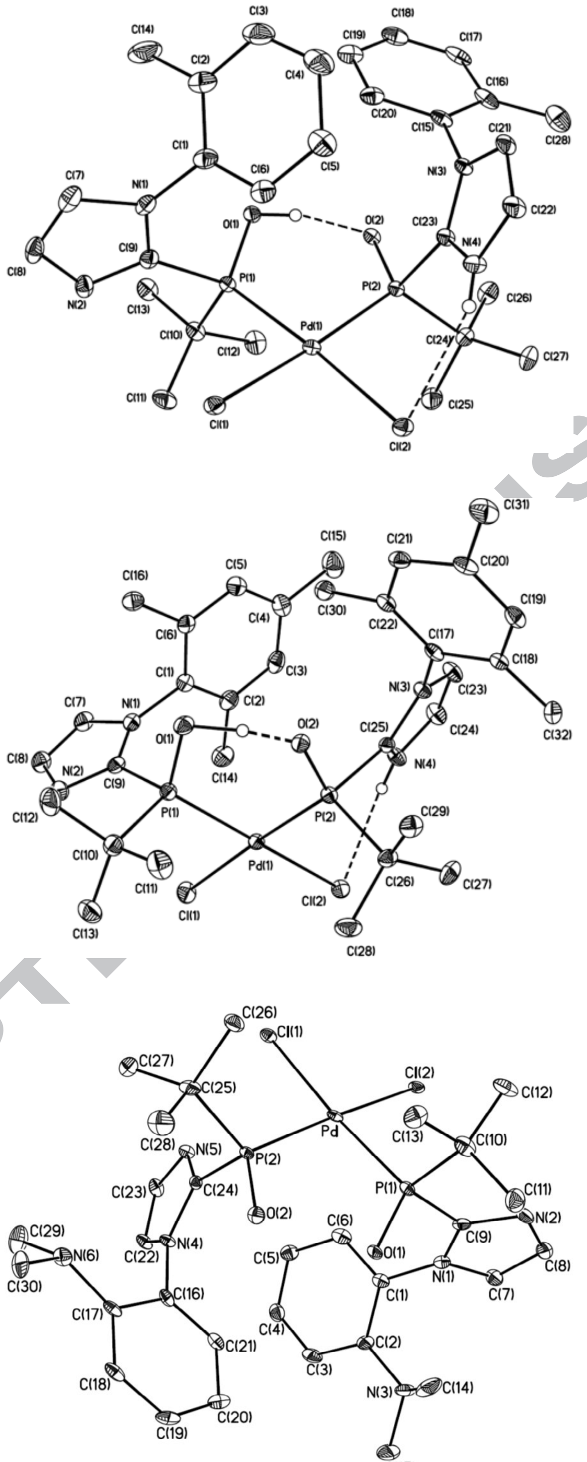


Figure 1. ORTEP drawings of **2Af'** (top), **2Ag'** (middle) and **2Ah'** (bottom). Most hydrogen atoms are omitted for clarity.

For comparison, the selected structural data of several related compounds are listed in Table 1. Except for **2Ah’**, the distances between the protonated N and the closest X (X = Cl, Br) range from 3.047Å to 3.197 Å, those are shorter than the sums of their van der Waals radius. An intra-molecular hydrogen bond is present in either **2Af’** or **2Ag’** where the protonated imidazole ring titles away from chloride. Generally speaking, *trans*-form of *bis*-phosphine coordinated palladium complexes are presumably more stable than that of *cis*-form complexes in terms of less steric hindrance between two bulky ligands. Nevertheless, the fact that the *cis*-conformations are dominated here is most likely due to the existence of an intra-molecular hydrogen bond between two ligands. Moreover, the environments of the two coordinated phosphine ligands are not the same. The differences in the P-C(im) bond lengths range from 0.019 Å to 0.052 Å. The reason could be that the bonding between C(im) and P(2) can be regarded as a carbon-to-phosphorus dative bond after the imidazolophosphine is converted to a NHC-phosphenium in **2Ax’**.[26]

Table 1. . Selected bond lengths and distances for **2Af’**, **2Ag’** and **2Ah’**.

	N···Cl	N-H	Cl···H	N-H···Cl	P(1)-C(im)	P(2)-C(im)
2Af’	3.164	0.77(4)	2.476	148.76	1.806(3)	1.858(3)
2Ag’	3.083	0.85(3)	2.334	148.77	1.813(3)	1.858(2)
2Ah’	3.710	0.8800	3.871	73.00	1.828(7)	1.847(6)

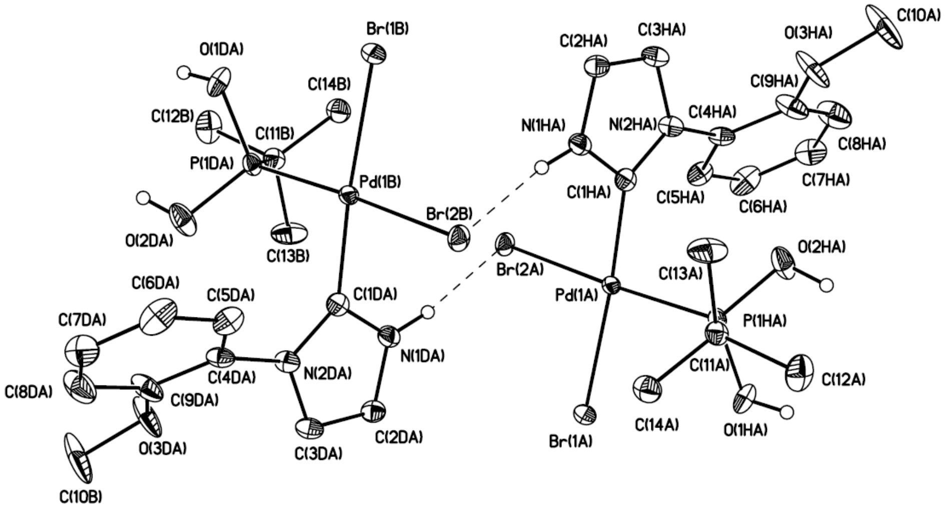


Figure 2. ORTEP drawing and the crystal packing of **3Bb**.

Unexpectedly, a unique palladium complex, **3Bb** was obtained from the reaction of **1b** with $PdBr_2$. This square planar palladium complex is consisted of two coordinated ligands, di-tert-butylphosphonous acid and a *3H*-NHC carbene, as well as two bromides all in *cis*-positions. We believe that the formation of **3Bb** was from a series of chemical conversions of **2Bb**.[17] Firstly, the tautomerization of **2Bb** to **2Bb’** *via* intra-molecular proton transfer. Subsequently, the nucleophilic attack of H_2O on phosphorus atom followed by intra-molecular deprotonation reaction of the reacted

H_2O by $P\text{-}O^-$ moiety. Next, the dissociation of the spectating **1Bb**, and eventually, the cleavage of the P-C(im) bond from the coordinated **1Bb**. To our knowledge, the case of **3Bb** is among the few examples of palladium complexes having both coordinating phosphine and carbene ligands directly from cleavage of the P-C(im) bond of an imidazole substituted SPO.[27] As shown, there are inter-molecular hydrogen bonding between the protonated nitrogen atoms and the bromides from two neighboring molecules (N…Br = 3.346 Å) in solid state (Figure 2).

An interesting observation was the formation of carbene-amine-coordinated **4Ah**, which was obtained from the crystal-growing process of the resulted solution from the reaction of **1h** with $Pd(COD)Cl_2$. The identification of **4Ah** was validated by the X-ray diffraction methods (Figure 3). It is obvious that the release of the $P(OH)_2(^tBu)$ ligand from **3Ah**, the counterpart of **3Bb**, creates a vacuum site for the potential coordination by nitrogen atom from N,N-dimethylaniline moiety in **3Ah**. As revealed in Figure 3, the palladium metal center is coordinated by both carbene and amine moieties in **4Ah**. Alternatively, **4Ah** can be regarded as a $PdCl_2$ skeleton being chelated by a κ^2-C,N-bidentate ligand. Judging from the composition of **4Ah**, only one molar equivalent of **1h** is required to form the complex, although the reaction was started with two molar equivalents of **1h**.

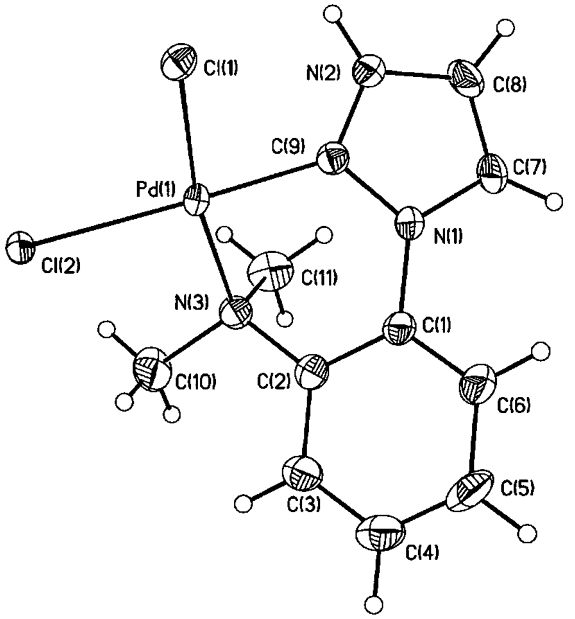


Figure 3. ORTEP drawing of **4Ah**.

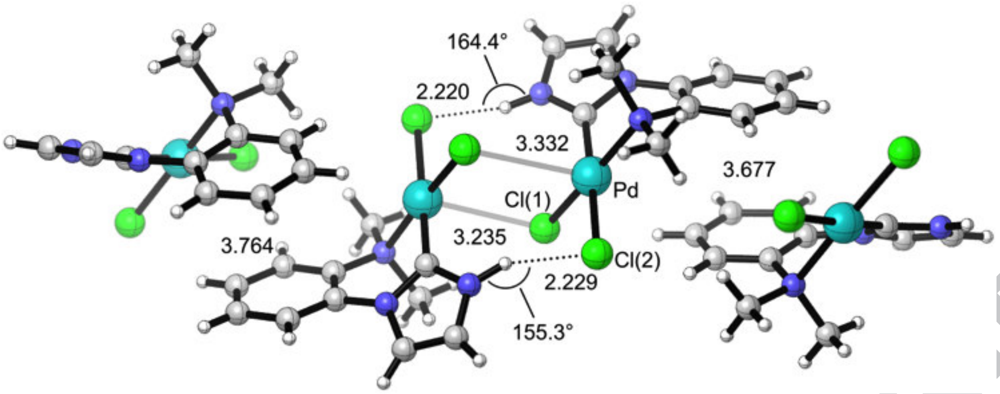
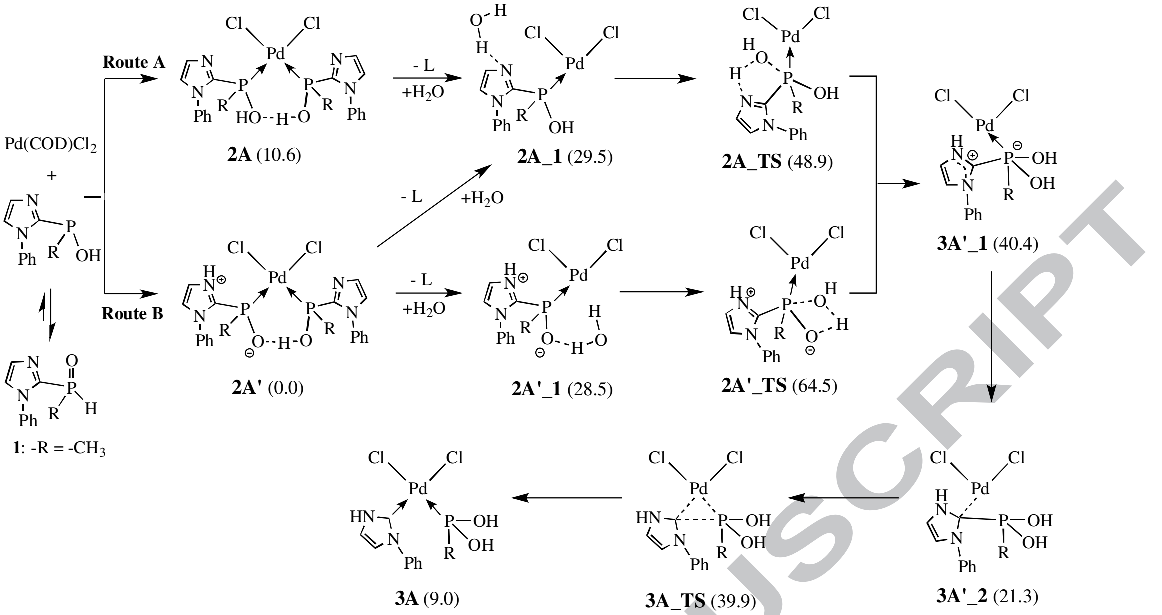


Figure 4. Depicted solid-state packing motif of **4Ah’**.

DFT studies of the reaction pathways for the formation of 3Aa using model pre-ligand SPO-Im 1

Detailed analysis of the crystal structure of **4Ah** indicates that non-covalent interactions play essential roles in the solid-state packing motif, including π-π, hydrogen-bond and long-distant ligand-to-metal interactions (Figure 4). It is revealed that, along the unit cell *a*-axis, parallel-displaced π-π interaction between two inter-molecularly adjacent phenyl rings have center-to-center distances of 3.764 and 3.677 Å, which are in the range of normal aromatic π-π stacking.[28] Along the *c*-axis, a molecular dimer mutually forms two inter-molecular hydrogen bonds via the Cl(2) and hydrogen of N(2)’-H’ at distances of 2.229 and 2.220 Å (angles of N(2)’-H’···Cl(2)/N(2)-H···Cl(2)’ are 155.3 and 164.4^{o}), respectively. In the dimer, furthermore, there are two short contacts, 3.235 and 3.332 Å, between intermolecular Cl(1)···Pd’ and Cl(1)’···Pd atoms, respectively.

The density functional theory (DFT) methods were employed to evaluate the plausible mechanism for the P-C(im) bond cleavage of palladium-coordinated SPO-Im that leading to the formation of complex **3A**x (Scheme 4 and 5). To make computations more efficient and feasible, a simplified model for pre-ligand SPO-Im **1** (R = CH_3) was used in our DFT study. There are two reaction pathways, **Route A** & **B**, were proposed and evaluated. The major difference between these two pathways is the location of the proton of P-OH either on oxygen (model **2A**) or nitrogen atom (model **2A’**). The conformer **2A’** is energetically more stable than that of **2A** by 10.2 kcal/mol. This is consistent with the observation of solid-state structures of **2Af’**, **2Ag’** and **2Ah’**.



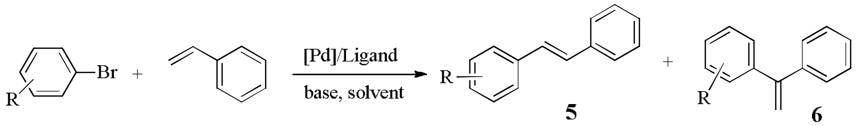
Scheme 5. Proposed reaction pathways for the formation of **3A**. Calculated free energies related to **2A'** are provided in parentheses in kcal/mol.

Subsequently, **2A_1** and **2A'_1** represent the tri-coordinated intermediates after the dissociation of one neutral PA-Im **1** ligand and picking up one H_2O molecule from surrounding. The source of water might come from the moisture that sneaked into the solution during the crystal-growing process. The incoming water shows hydrogen-bond interaction with nitrogen atom in complex **2A_1** or with oxygen atom in **2A'_1**. These two intermediates are energetically similar with each other. In **2A_TS**, one of the O-H bonds from water is breaking and the P-OH bond is forming simultaneously. Instead, the less energy-demanding process of **2A_1** to **3A'_1** via **2A_TS** ($\Delta G^{\ddagger}$ = 38.1 kcal/mol) than **2A'_1** to **3A'_1** via **2A'_TS** ($\Delta G^{\ddagger}$ = 37.4 kcal/mol) was elucidated by DFT calculations. The formation of a four-membered ring in **2A'_TS** is believed to be less favorable than forming a five-membered ring in **2A_TS**.

Thereafter, both **Route A** and **B** lead to the same conformation of a zwitterionic type intermediate **3A'_1**. The formation of P-C(im) bond that followed by the breaking of a P-Pd bond lead to **3A'_2**. This is an exothermic process (ΔG = -21.7 kcal/mol). Eventually, the conversion of **3A'_2** to the final product **3Aa** through the cleavage of a P-C(im) bond and formation of a P-Pd bond in **3Aa_TS** is achieved with a moderate activation energy of 18.4 kcal/mol. Consequently, the formation of **4Ah** from **3Ah** could be anticipated by the releasing of a $PR(OH)_2$ ligand from **3Ah** and followed by the coordination of amino group to the unsaturated palladium center.

Palladium-catalyzed Heck reactions using selected 1c~1l as ligands

As known, only small fraction of secondary phosphine oxide (SPO, RR'P(=O)H) might be converted to its less stable tautomeric form, phosphinous acid (PA, RR'POH), in solution unless strong electron-withdrawing substituent(s) is/are employed. Nevertheless, the formation of PA-coordinated metal complex is resulted in the presence of palladium salt even started with SPO. Recently, we reported the preparation of ligand (**1b**) and its application in cross-coupling reactions.[17] In this work we wish to extend the scope of these SPO-Im **1c**-**1l** as pre-ligands in transition-metal catalyzed Heck cross-coupling reactions (Scheme 6).

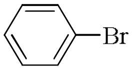
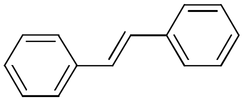
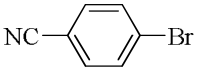
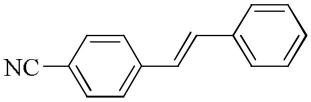
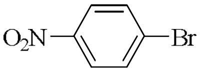
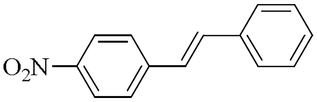
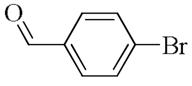
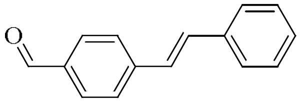
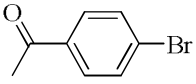
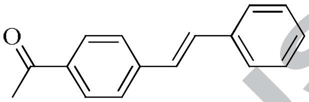
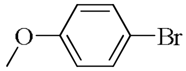
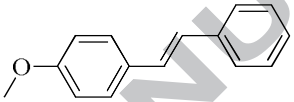
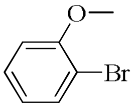
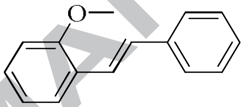
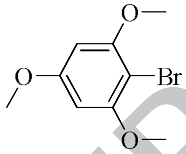
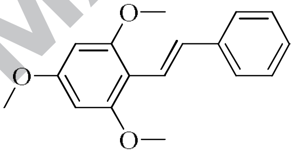
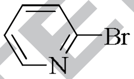
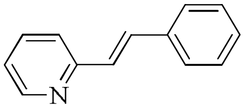


Scheme 6. Heck reactions were catalyzed by *in situ* combination of palladium salts with selected **1** as ligands.

To optimize the reaction conditions, a series of experiments under various reaction conditions in terms of base, solvent and reaction temperature for a model coupling reaction of styrenes and bromobenzenes were pursued. As known, Heck reaction normally requires more severe reaction condition than that of Suzuki reaction.[2b,29] Thereby, Heck reactions of substituted bromobenzene with styrene were carried out at elevated temperature using a high boiling point solvent DMF as the acting medium as shown in Scheme 6. For efficiency comparison with the reported work of Hayashi.[30] similar procedures for the catalytic reactions under investigation were carried out as follows. A suitable Schlenk tube was charged with 1.0 mmol of styrene, 1.1 mmol of bromobenzene, 2.0 mmol of base. Then, the combination of 2.0 mol % of palladium salt and 4.0 mol % of ligand as catalyst precursor was added. The mixture was stirred at a preset reaction temperature and time depending on the reaction executed. It was then followed by an acidic work-up. Due to steric hindrance, the formation of 1,2-disubstituted ethylene in *trans*-form (**5**) is predominated as the major product than that of *cis*-form. Meanwhile, 1,1'-disubstituted ethylene (**6**) is expected as a minor side product. After screening all the influential factors, it was concluded that the optimal reaction condition comes by using **1e**/$Pd(Oac)_2$ (2 mol%) as the catalyst precursor with the combination of K_2CO_3 (2.0 mmol) in DMF (1.0 mL) and reacting at 90 ^{o}C for 12 h.[31]

The scope of this Heck coupling reaction using various aryl bromides was examined by employing the optimized condition from the previous studies. The results are presented in Table 2. As shown, compatible efficiencies were obtained for either employing electron-withdrawing or -donating group substituted arylbromides (Entries 1-6). Besides, small amount of side products either from self-coupling of arylbromide or 1,1'-disubstituted ethylene were observed, thus also lessens the conversion rate. Moderate performance was observed for the case having -OMe on *ortho*-position of arylbromide probably due to steric hindrance (Entry 7). No conversion was observed for either with severe hindrance case such as 2-bromo-1,3,5-trimethoxybenzene (Entry 8) or heterocyclic case such as 2-bromopyridine (Entry 9).

Table 2. Heck reactions employed various substrates[a]

Entry	Substate	Product	Yield(%)[b, c]
1			98(99:1)
2			93(100:0)
3			98(97:3)
4			94(100:0)
5			92(100:0)
6			90(97:3)
7			67(97:3)
8			0
9			0

[a] Conditions: 1.1 mmol arylbromide, 1.0 mmol styrene, 2.0 mmol K_2CO_3, 1 mL DMF (dried), 0.02 mmol $Pd(OAc)_2$, 0.04 mmol **1e**, 90 °C, 12 h; [b] Total isolated yield; [c] In parentheses, the ratio of **5** with **6** was determined by ^1H NMR.

Conclusions

Several new air- and moisture-stable imidazolio-secondary phosphine oxides (SPO-Im, **1c**-**1l**) were prepared and applied in palladium-catalyzed Heck cross-coupling reactions. Excellent efficiencies were shown for various styrene derivatives towards aryl bromides. Several functional groups and heteroaryl were tolerated in this reaction. The formation of unexpected carbene coordinated palladium complexes, **3Bb** and **4Ah**, from the reactions of corresponding SPO-Im **1b** and **1h** with palladium salts is noteworthy and the reaction pathways for the formations of NHC-phosphite coordinated pallasium complex **3Bb** has been proposed based on the characterized structures of **2Af'**, **2Ag'** and **2Ah'**. By using model pre-ligand SPO-Im **1**, the reaction mechanism for the formation of **3Bb** analogue was also investigated with DFT calculations.

Experimental Section

General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-flushed glove box. Freshly distilled solvents were used. All processes of separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924) or column chromatography. GC-MS analysis was performed on an Agilent 5890 gas chromatograph (Restek Rtx-5MS fused silica capillary column: 30m, 0.25mm, 0.5μm) with an Agilent® 5972 mass selective detector. Routine ^{1}H NMR spectra were recorded on a Varian-400 spectrometer at 399.756 MHz. The chemical shifts are reported in ppm relative to internal standards TMS (δ = 0.0 ppm). ^{31}P and ^{13}C NMR spectra were recorded at 161.835 and 100.529 MHz, respectively. The chemical shifts for the former and the latter are reported in ppm relative to internal standards H_3PO_4 (δ = 0.0 ppm) and $CHCl_3$ (δ = 77.0 ppm) or CH_2Cl_2 (δ = 53.0 ppm), respectively. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Electrospray ionization-high resolution mass spectra (ESI-HRMS) were recorded on a Finnigan/Thermo Quest Mat 95 XL mass spectrometer.

Synthesis and characterization of substituted 2-(tert-butylhydrophosphoryl)-1-phenyl-1H-imidazole derivatives (1c-1l)

A N_2 flashed 100 ml round-bottomed flask was placed 25 mL THF with 5.0 mmol of 1-(3-methoxyphenyl)-1*H*-imidazole (0.869 g), which was prepared by procedures reported elsewhere.[17] The solution had been cooled to -78 °C before 2.2 mmol of *n*-BuLi (0.88 mL, 2.5 M in hexane) was added. The suspension was slowly warmed up to 0 °C and stirred for another 30 minutes. Subsequently, the solution was slowly transferred to another flask which contained 5.5 mmol of *tert*-butyldichlorophosphine (0.869 g) in 25 mL THF at 0 °C. The reaction mixture was then heated up gradually from 0 °C to 50 °C, and stirred for another 2 hours. After completion, the solution was diluted with 50 mL ethyl acetate and the organic layer was collected. It was again extracted twice with ethyl acetate (2 x 5 mL). Then, the combined organic layer was dried with $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography by changing the polarity of mixed solvent. It was started from ethyl acetate/n-hexane=1:3 then to pure ethyl acetate and finally to ethyl acetate/methanol=20:1. The isolated white solid **1c** (0.598 g, 2.15 mmol) was obtained in 43% yield.

Similar procedures as the preparation of **1c** were applied to the syntheses of substituted 2-(*tert*-butylhydrophosphoryl)-1*H*-imidazole derivatives (**1d-1l**) starting from each corresponding substituted imidazoles. The yields of purified **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, and **1l** are 43 %, 72 %, 50 %, 41 %, 51 %, 49 %, 23 %, 5-10%, 18 %, respectively.

‡ Spectroscopic data for **1c** ^{1}H NMR (CDCl$_3$, δ/ppm): 7.32 (d, *J* = 8.0 Hz, 1H, Ar), 7.27 (1H, Imidazole), 7.24 (1H, Imidazole), 7.20 (1H, Ar), 7.17 (t, *J* = 24.0 Hz, 1H, Ar), 7.10 (d, J_{P-H} = 484 Hz, 1H, P-H), 7.06 (d, *J* = 8.0 Hz, 1H, Ar), 6.93 (d, *J* = 8.0 Hz, 1H, Ar), 3.87 (s, 3H, OCH$_3$), 1.12 (d, *J* = 16.0 Hz, 9H, C(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, δ/ppm): 139.5 (d, J_{P-H} = 125.8 Hz, 1C, Imidazole), 137.5, 130.4 (2C, Imidazole) , 158.8, 130.3, 124.6, 117.1, 114.9, 111.1 (6C, Ar), 55.3 (1C, OMe), 32.4 (d, J_{P-C} = 70.4 Hz, 1C, ^{t}Bu), 23.4 (3C, ^{t}Bu); ^{31}P NMR (CDCl$_3$, δ/ppm): 32.2 ppm (d, J_{P-H} = 482 Hz).

‡ Spectroscopic data for **1d** ^{1}H NMR (CDCl$_3$, δ/ppm): 7.40 (d, *J* = 8.0 Hz, 2H, Ar), 7.23 (s, 1H, Imidazole), 7.17 (s, 1H, Imidazole), 6.99 (d, J_{P-H} = 480 Hz, 1H, P-H), 6.91 (d, *J* = 6.0 Hz, 2H, Ar), 3.77 (s, 3H, OCH$_3$), 1.02 (d, *J* = 16.0 Hz, 9H, ^{t}Bu); ^{13}C NMR (CDCl$_3$, δ/ppm): 139.8 (d, J_{P-C} = 130.7 Hz, 1C, Imidazole), 130.4, 130.3 (2C, Imidazole), 159.7, 127.1, 125.2, 125.2, 122.9, 114.6, 114.2 (6C, Ar), 55.3 (1C, OMe), 32.4 (d, J_{P-C} = 70.0 Hz, 1C, ^{t}Bu), 23.4 (3C, ^{t}Bu); ^{31}P NMR (CDCl$_3$, δ/ppm): 32.1 ppm (d, J_{P-H} = 480 Hz).

‡ Spectroscopic data for **1e** ^{1}H NMR (CDCl$_3$, δ/ppm): 7.37 (1H, Imidazole), 7.02 (1H, Imidazole), 6.88 (d, J_{P-H} = 476 Hz, 1H, P-H), 6.17 (s, 2H, Ar), 3.85 (s, 3H, OCH$_3$), 3.76 (s, 3H, OCH$_3$), 3.75 (s, 3H, OCH$_3$), 1.15 (d, *J* = 16.0 Hz, 9H, ^{t}Bu); ^{13}C NMR (CDCl$_3$, δ/ppm): 139.8 (d, J_{P-C} = 130.7 Hz, 1C, Imidazole), 130.1, 125.8 (2C, Imidazole), 161.8, 156.5, 156.1 107.3, 90.4 (6C, Ar), 55.8, 55.3, (3C, OMe), 32.2 (d, J_{P-C} = 80.4 Hz, 1C, ^{t}Bu), 23.1 (3C, ^{t}Bu); ^{31}P NMR (CDCl$_3$, δ/ppm): 28.0 ppm (d, J_{P-H} = 476 Hz).

‡ Spectroscopic data for **1f** ^{1}H NMR (CDCl$_3$, δ/ppm): 7.41-7.31 (m, 5H, Ar and Imidazole), 7.16 (s, 1H, Imidazole), 6.89 (d, 1H, P-H, J_{P-H} = 474 Hz), 2.14 (s, 3H, Me), 1.19 (d, *J* = 18.0 Hz, 9H, ^{t}Bu); ^{13}C NMR (CDCl$_3$, δ/ppm): 140.0 (d, J_{P-C} = 126.0 Hz, 1C, Imidazole), 135.76, 135.28 (2C, Imidazole), 131.03, 130.81, 129.86, 127.88, 126.60, 124.96 (6C, Ar), 32.38 (d, J_{P-C} = 73.0 Hz, 1C, ^{t}Bu), 23.50 (3C, ^{t}Bu), 17.30 (1C, Me); ^{31}P NMR (CDCl$_3$, δ/ppm): 28.8 (d, J_{P-H} = 472 Hz).

‡ Spectroscopic data for **1g** ^{1}H NMR (CDCl$_3$, δ/ppm): 7.43 (1H, Imidazole), 7.04 (1H, Imidazole), 6.99 (1H, Ar), 6.96 (1H, Ar), 6.65 (d, 1H, P-H, J_{P-H} = 472 Hz), 2.34 (3H, *p*-Me), 2.07 (3H, *o*-Me), 1.95 (3H, *o*-Me), 1.30 (d, *J* = 18.0 Hz, 9H, ^{t}Bu); ^{13}C NMR (CDCl$_3$, δ/ppm): 140.73 (d, J_{P-C} = 127.0 Hz, 1C, Imidazole), 139.62, 136.20 (2C, Imidazole), 134.84, 132.49, 131.30 , 129.45, 128.91, 123.96 (6C, Ar), 32.27 (d, J_{P-C} = 74.4 Hz, 1C, ^{t}Bu), 23.62 (3C, ^{t}Bu), 21.07, 17.52 (3C, Me); ^{31}P NMR (CDCl$_3$, δ/ppm): 24.8 (d, J_{P-H} = 472 Hz).

‡ Spectroscopic data for **1h** ^{1}H NMR ($CDCl_3$, δ/ppm): 7.40~7.35 (m, 2H, Ar), 7.29 (s, 1H, Imidazole), 7.24 (1H, Imidazole), 7.09~7.02 (m, 2H, Ar), 6.74 (d, 1H, P-H, $J_{P\text{-}H}$ = 532 Hz), 2.48 (6H, Nme_2), 1.20 (d, J = 20.0 Hz, 9H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, δ/ppm): 140.1 (d, $J_{P\text{-}C}$ = 120.6 Hz, 1C, Imidazole), 147.97, 130.9 (2C, Imidazole), 129.8, 128.6, 127.5, 126.37, 123.5, 121.6, 118.9 (6C, Ar), 42.0 (2C, Nme_2), 32.2 (d, $J_{P\text{-}C}$ = 70.4 Hz, 1C, ^{t}Bu), 23.3 (3C, ^{t}Bu); ^{31}P NMR ($CDCl_3$, δ/ppm): 25.5 ppm (d, $J_{P\text{-}H}$ = 532 Hz).

‡ Spectroscopic data for **1i** ^{1}H NMR ($CDCl_3$, δ/ppm): 7.33 (s, 1H, Imidazole), 7.31 (s, 1H, Imidazole), 7.28 (d, J = 4.0 Hz, 1H, Ar), 7.00 (s, 1H, Ar), 6.95 (d, 1H, P-H, $J_{P\text{-}H}$ = 495 Hz), 6.76 (t, J = 8.0 Hz, 1H, Ar), 3.02 (6H, Nme_2), 1.13 (d, J = 20.0 Hz, 9H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, δ/ppm): 140.2 (d, $J_{P\text{-}C}$ = 130.7 Hz, 1C, Imidazole), 137.8, 130.5 (2C, Imidazole), 151.1, 130.4, 129.9, 124.8, 112.4, 112.3, 109.9 (6C, Ar), 40.3 (2C, Nme_2), 32.7 (d, $J_{P\text{-}C}$ = 70.0 Hz, 1C, ^{t}Bu), 23.8 (3C, ^{t}Bu); ^{31}P NMR ($CDCl_3$, δ/ppm): 31.2 ppm (d, $J_{P\text{-}H}$ = 495 Hz).

‡ Spectroscopic data for **1j** ^{1}H NMR ($CDCl_3$, δ/ppm): 7.33 (d, 1H, P-H, J = 8.0 Hz, Ar), 7.27 (1H, Imidazole), 7.18 (1H, Imidazole), 7.00 (d, 1H, P-H, $J_{P\text{-}H}$ = 476 Hz), 6.70 (d, 1H, P-H, J = 8.0 Hz, Ar), 2.97 (6H, Nme_2), 1.08 (d, J = 16.0 Hz, 9H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, δ/ppm): 140.0 (d, $J_{P\text{-}C}$ = 130.0 Hz, 1C, Imidazole), 130.3, 130.2 (2C, Imidazole), 150.5, 126.7, 125.3, 111.8 (6C, Ar), 40.2 (2C, Nme_2), 32.4 (d, $J_{P\text{-}C}$ = 6.0 Hz, 1C, ^{t}Bu), 23.6 (3C, ^{t}Bu); ^{31}P NMR ($CDCl_3$, δ/ppm): 31.1 ppm (d, $J_{P\text{-}H}$ = 476 Hz).

‡ Spectroscopic data for **1k** ^{1}H NMR ($CDCl_3$, δ/ppm): 7.48 (t, J = 8.0 Hz, 1H, Ar), 7.42 (1H, Imidazole), 7.31 (d, J = 8.0 Hz, 1H, Ar), 7.25 (d, J = 8.0 Hz, 1H, Ar), 7.07 (s, 1H, Imidazole), 6.60 (d, 1H, P-H, $J_{P\text{-}H}$ = 464 Hz), 2.50-2.42 (m ,1H, $C\underline{H}Me_2$), 2.23-2.15 (m ,1H, $C\underline{H}Me_2$), 1.37, 1.32 (d, J = 18.0 Hz, 9H, ^{t}Bu), 1.30 (d, J = 8.0 Hz, 3H, $CH(C\underline{H}_3)_2$), 1.20 (d, J = 8.0 Hz, 3H, $CH(C\underline{H}_3)_2$), 1.09 (d, J = 8.0 Hz, 3H, $CH(C\underline{H}_3)_2$), 1.06 (d, J = 8.0 Hz, 3H, $CH(C\underline{H}_3)_2$); ^{13}C NMR ($CDCl_3$, δ/ppm): 141.33 (d, $J_{P\text{-}C}$ = 127.0 Hz, 1C, Imidazole), 147.25, 145.59 (2C, Imidazole), 131.68, 130.73, 130.59, 125.48, 124.37, 123.58 (6C, Ar), 31.69 (d, $J_{P\text{-}C}$ = 75.0 Hz, 1C, ^{t}Bu), 28.46, 28.24, 26.06, 25.98, 3.74 (6C, ^{i}Pr), 22.72, 22.43 (3C, ^{t}Bu); ^{31}P NMR ($CDCl_3$, δ/ppm): 22.4 (d, $J_{P\text{-}H}$ = 464 Hz).

‡ Spectroscopic data for **1l** ^{1}H NMR ($CDCl_3$, δ/ppm): 8.57 (d, J = 8.0 Hz, 1H, Ar), 7.91~7.89 (m, 2H), 7.66 (1H, Imidazole), 7.41 (d, 1H, P-H, $J_{P\text{-}H}$ = 496 Hz), 7.39~7.35 (m, 2H), 1.20 (d, J = 20.0 Hz, 9H, ^{t}Bu); ^{13}C NMR ($CDCl_3$, δ/ppm): 139.1 (d, $J_{P\text{-}C}$ = 120.0 Hz, 1C, Imidazole), 149.2, 148.9 (2C, Imidazole), 130.8, 130.7, 123.5, 122.9, 117.9 (6C, Ar), 33.0 (d, $J_{P\text{-}C}$ = 0.0 Hz, 1C, ^{t}Bu), 23.88 (3C, ^{t}Bu); ^{31}P NMR ($CDCl_3$, δ/ppm): 34.5 ppm (d, $J_{P\text{-}H}$ = 496 Hz).

Reactions of substituted 2-(tert-butylhydrophosphoryl)-1-phenyl-1H-imidazole derivatives with palladium halides

Under nitrogen, a 20 mL Schlenk tube with stir bar was charged with 1 mL of THF, 0.02 mmol of Pd[COD]Cl_2 and 2 molar equivalents of (*t*-butylhydrophosphoryl)-1-*o*-tolyl-1*H*-imidazole (**1f**). The solution was stirred at 60 °C (or 25 °C for **1h**) for 2 hours. The solution was cooled down to room temperature and solvent was completely removed under reduced pressure. The residue was completely dissolved in 1 mL of CH_2Cl_2; then, 1 mL of n-hexane was added gradually. Crystals of **2Af'** with suitable size for x-ray diffraction were obtained after placing the solution at 4 ^{o}C for several days. Similar procedures were taken for preparing **2Ag'** and **2Ah'** from corresponding **1g** and **1h**, respectively. Crystals of **3Bb** were obtained from the side reaction of **1b** with PdBr$_2$. Crystals of **4Ah** were obtained presumably from the conversion of **2Ah'**. Nevertheless, almost all of **2Ah'** was converted to **4Ah** after purification process by column chromatography. Therefore, it is not enough sample of **2Ah'** for characterization by spectroscopic methods.

‡ Spectroscopic data for **2Af'** ^{1}H NMR (CDCl$_3$, δ/ppm): 13.86 (b, 1H, N-H), 7.72 (s, 2H), 7.53 (d, *J* =7.6 Hz, 2H), 7.18~7.11 (m, 6H), 7.04 (s, 2H), 2.1 6(s, 6H, CH$_3$), 1.36 (d, *J* =12.4 Hz, 18H, *t*-Bu); ^{13}C NMR (DMSO-d^6, δ/ppm): 142.5 (d, *J* = 48.0 Hz), 135.9, 130.9, 130.0, 129.4, 128.4, 127.4, 126.8, 126.0, 27.8, 17.9 (d, *J* = 95.8 Hz), 17.7; ^{31}P NMR (CDCl$_3$, δ/ppm): 92.7.

‡ Spectroscopic data for **2Ag'** ^{1}H NMR (CDCl$_3$, δ/ppm): 8.15 (b, 1H, N-H), 6.94(s, 2H), 6.87(s, 2H), 6.83(s, 2H), 6.78(s, 2H), 2.21(s, 6H) , 2.09(s, 6H), 1.92(s, 6H), 1.38(d, *J* = 16.8 Hz, 18H, *t*-Bu); ^{13}C NMR (CDCl$_3$, δ/ppm): 143.8, 143.3, 139.1, 136.3, 135.2, 133.0, 129.5, 129.0, 128.8, 126.8, 124.7, 41.6, 41.3, 27.8, 27.4, 21.1, 21.0, 19.4, 18.0; ^{31}P NMR (CDCl$_3$, δ/ppm): 97.8.

‡ Spectroscopic data for **3Bb** ^{1}H NMR (CDCl$_3$, δ/ppm): 11.72 (s, 1H, N-H), 8.72 (d, *J* = 7.6 Hz, 1H, Ar), 7.49 (t, *J* = 11.2 Hz, 1H, Ar), 7.38 (t, *J* = 2.0 Hz, 1H, Ar), 7.31 (t, *J* = 2.0 Hz, 1H, Ar), 7.25 (t, *J* = 7.2 Hz, 1H, Ar), 7.05 (d, *J* = 8.4 Hz, 1H, Ar), 3.84 (s, 3H, OMe), 0.77 (d, *J* = 8.0 Hz, 9H, ^{t}Bu); ^{13}C NMR (CDCl$_3$, δ/ppm): 154.4 (NHC), 152.4, 130.6, 128.8, 127.4, 124.7, 121.7, 120.0, 111.7 (Aromatic), 55.7 (OMe), 37.4(d, *J* = 56, ^{t}Bu, *ipso*), 23.6(^{t}Bu, CH$_3$); ^{31}P NMR (CDCl$_3$, δ/ppm): 127.8.

‡ Spectroscopic data for **4Ah** ^{1}H NMR (CDCl$_3$, δ/ppm): 8.39 (s, 1H, N-CH=C), 7.56 (s, 1H, N-CH=C), 7.33 (t, *J* = 8.0 Hz, 1H, Ar), 7.15 (d, *J* = 12.0 Hz, 1H, Ar), 7.08 (d, *J* = 8.0 Hz, 1H, Ar), 7.01 (t, *J* = 6.0 Hz, 1H, Ar), 6.30 (s, 1H, C-NH-C), 2.50 (s, 6H, N-(CH$_3$)$_2$). ^{13}C NMR (CDCl$_3$, δ/ppm): 42.37 (s, N-(CH$_3$)$_2$), 116.70, 119.35, 119.22, 116.70, 126.26, 129.72 (s, Ar), 139.31, 129.88 (s N-CH=CH), 147.58 (s, N-C-N); MS (EI, m/z): 187.1 (M-PdCl$_2$)$^+$.

General procedure for the Heck reactions

Schlenk tube was charged with Pd(Oac)$_2$ (0.03 mmol, 0.0067 g), ligand (0.06 mmol) and salt (3 mmol). This tube was subjected to vacuum for 10 minutes and then toluene (1 mL) was added. To this mixture styrene (1.2 mmol, 0.137 mL) and aryl bromide (1.0 mmol) were added slowly with the help of syringe. The resulting suspension was stirred at 90 ^{o}C for 12 hours. After completion of reaction, the solution was diluted with EtOAc and filtered through a pad of Celite. The organic layer was then extracted with ethylacetate (10 x 3 mL) and water. The organic layer was collected separately and dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure to obtain crude residue. The product was purified by flash chromatography (5% EtOAc/hexane), which yielded mostly the desired *trans*-stilbene.

X-ray crystallographic studies

Suitable crystals of **2Af'**, **2Ag'**, **2Ah'**, **3Bb** and **4Ah** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART

1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[32] All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.[33]

Computational methods

All calculations were done with *Gaussian* 09.[34] Gas-phase geometry optimizations were done with the M06 density functional.[35] For palladium, the LANL2DZ(f) effective core potential in conjunction with the corresponding basis set of double zeta quality augmented it with a set of f functions was employed; while for the other atoms, the 6-31G(d,p) was used (denoted as 631LAN(f)). Frequency calculations were performed so as to verify whether the optimized geometries were local minima (no imaginary frequency) or transition states (one imaginary frequency) at the same level of theory. Considering the solvation effect of THF with PCM solvation model,[36] the subsequent single-point calculations were performed at the M06/631+LAN(f) level of theory in which the 6-31+G(d,p) basis set was employed for non-metal atoms instead of 6-31G(d,p). Free energy for each species in THF solution was estimated with the sum of PCM energy ($G_{(631+LAN(f))}$) and the zero-point vibrational energy plus the gas-phase thermal correction to enthalpy ($G_{corr} = H_{corr} - TS_{tot}$) obtained at the M06/631LAN(f) level. Accordingly, relative free energies were calculated to construct the potential energy surface of the formation of the NHC-coordinated complex **3A** from the reaction of SPO-Im and Pd(COD)Cl_2.

Appendix A. Supplementary data

CCDC 901014, 901015, 901016, 901017, and 901018 contain the supplementary crystallographic data for **2Af'**, **2Ag'**, **2Ah'**, **3Bb** and **4Ah**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Imidazolio-substituted Secondary Phosphine Oxides as Carbene Precursor

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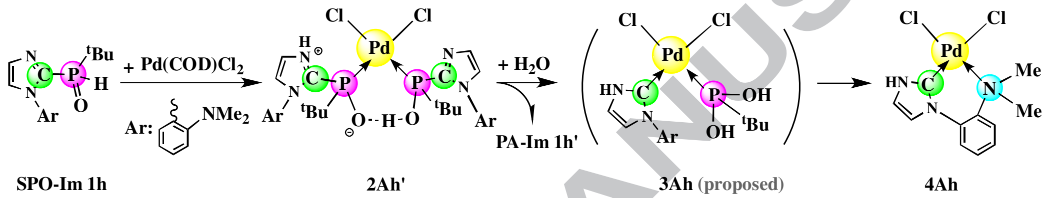
Graphical abstract:



Imidazolio-substituted Secondary Phosphine Oxides as Carbene Precursor

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Synopsis:

The reaction of SPO-Im **1h** with Pd(COD)Cl_2 yielded a *bis*-**1h’** (PA-Im) coordinated *cis*-palladium dichloride complex, **2Ah’**. It subsequently converted to a carbene coordinated palladium complex, **3Ah**, in the presence of moisture, and eventually to **4Ah**. The P-C(imidazole) bond of **1h’** was dissected and the dissociated species acted as a NHC carbene ligand towards palladium metal.